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(54) **Title of the invention**

Method for the production of multilayered styrene copolymer, multilayered styrene copolymer and molded product of multilayered styrene copolymer

(57) **Summary**

Problem

To present method for the production of multilayered styrene copolymer that gives molded products with excellent transparency, color development and impact strength and, molded product of multilayered styrene copolymer.

Solution

Method for the production of multilayered styrene copolymer that consists of the following steps (1) ~ (5) (the composition is such that the quantity of vinyl silane compound is 0.1 weight % or more in steps (1) ~ (5)), and molded product of the copolymer.

(1): Conducting emulsion polymerization of monomer mixture containing styrene.

(2): Conducting emulsion polymerization of monomer mixture (b) in presence of the copolymer (A) obtained in step (1) above.

(3): Conducting emulsion polymerization of monomer mixture (c) containing styrene, in presence of copolymer (B) obtained in step (2).

(4): Conducting emulsion polymerization of monomer mixture (d) containing styrene, in presence of copolymer (C) obtained in step (3).

(5): Conducting emulsion polymerization of monomer mixture (e) containing styrene, in presence of copolymer (D) obtained in step (4) to get the copolymer (E).

Scope of the patent application

Claim 1

Method for the production of multilayered styrene copolymer that consists of the following steps (1) ~ (5) (in case of vinyl silane compounds, the quantity is 0.1 weight % or more, in steps (1) ~ (5)), and molded product of the copolymer.

(1): Monomer mixture (a) composed of 40 ~ 99.999 weight % of styrene and 0 ~ 35 weight % of atleast one selected from (metha) acrylate ester (having 1 ~ 8 carbon atoms) and vinyl cyanide compound, 0.001 ~ 5 weight % of multifunctional group monomer and 0 ~ 20 weight % of a vinyl silane compound (that can copolymerize with these) is compounded in such a way that glass transition temperature of the copolymer (A) thus obtained by emulsion polymerization is more than 0°C.

(2): Monomer mixture (b) composed of 75 ~ 99.949 weight % of (metha) acrylate ester (having 1 ~ 8 carbon atoms) and 0.001 ~ 5 weight % of multifunctional group monomer and 0 ~ 20 weight % of a vinyl silane compound (that can copolymerize with these) is compounded in such a way that the glass transition temperature of the copolymer (B) thus newly obtained in this step (2) by emulsion polymerization in presence of the copolymer (A) (obtained in step (1) above), is less than 0°C.

(3): Monomer mixture (c) composed of styrene, 0 ~ 99.999 weight % of at least one selected from (metha) acrylate ester (having 1 ~ 8 carbon atoms) and vinyl cyanide compound, 0.001 ~ 99.95 weight % of multifunctional group monomer and 0 ~ 20 weight % of a vinyl silane compound (that can copolymerize with these) is compounded in such a way that glass transition temperature of the copolymer (C) thus newly obtained in this step (3) in presence

of the copolymer (B) (obtained in step (2) above), is more than $0^{o}C$ and the refractive index is in the range of 1.45 ~ 1.60.

(4): Monomer mixture (d) composed of 60 ~ 85 weight % of styrene and 15 ~ 40 weight % vinyl cyanide compound, 0 ~ 15 weight % (metha) acrylate ester (having 1 ~ 8 carbon atoms) and 0.001 ~ 10 weight % of multifunctional group monomer and 0 ~ 20 weight % of a vinyl silane compound (that can copolymerize with these) is compounded and emulsion-polymerized in presence of the copolymer (C) (obtained in step (3) above), to get new copolymer (D).

(5): Monomer mixture (e) composed of 60 ~ 90 weight % of styrene and 10 ~ 35 weight % of vinyl cyanide compound, 0 ~ 30 weight % (metha) acrylate ester (having 1 ~ 8 carbon atoms) and, 0 ~ 20 weight % of a vinyl silane compound (that can copolymerize with these) is compounded and emulsion polymerized to get new copolymer (E).

Claim 2

Method of production of multilayered styrene copolymer mentioned in Claim 1 above, in which the composition of respective monomer mixtures (a) ~ (e) from steps (1) ~ (5) per total of (a) ~ (e) is as follows. Monomer mixture (a) 5 ~ 55 weight %, monomer mixture (b) 10 ~ 60 weight %, monomer mixture (c) 1 ~ 20 weight %, monomer mixture (d) 5 ~ 35 weight % and monomer mixture (e) 10 ~ 79 weight %.

Claim 3

Method of production of multilayered styrene copolymer mentioned Claim 1 or 2 above, in which the particle diameter of copolymer (E) at the end of step (5) is 50 ~ 500 nm.

Claim 4

Method of production of multilayered styrene copolymer mentioned in any of the Claims 1 ~ 3 above, in which the vinyl group of vinyl silane compound is methacryl group or acryl group.

Claim 5

Method of production of multilayered styrene copolymer mentioned in any of the Claims 1 ~ 4 above, in which the silane compound is dimethyl siloxane, phenyl siloxane or methyl phenyl siloxane.

Claim 6

Method of production of multilayered styrene copolymer mentioned in any of the Claims 1 ~ 5 above, in which the multifunctional monomer compounded in steps (1) ~ (4) is at least one selected from the following group- Polyethylene glycol, polypropylene glycol, (metha) acrylate ester of alkylene diol and di-vinyll benzene.

Claim 7

Method of production of multilayered styrene copolymer mentioned in any of the Claims 1 ~ 6 above, in which the multifunctional monomer compounded in step (4) is allyl methacrylate.

Claim 8

Multilayered styrene copolymer obtained by the method of production of multilayered styrene copolymer mentioned in any of the Claims 1 ~ 7 above.

Claim 9

Molded product of multilayered styrene copolymer obtained by using multilayered styrene copolymer mentioned in Claim 8 above.

Detailed description of the invention

[0001] **Technical fields related to this invention**

This invention is concerned with multilayered styrene copolymer that gives transparent molded products, has excellent weather resistance, impact strength, and has especially good impact strength at low temperatures and, method of production of such multilayered styrene copolymer and its molded product.

[0002] **Conventional methods**

Thermoplastic resin rubber called as ABS is an impact resistant resin. However, the butadiene polymer used for imparting impact strength to ABS resin has many chemically unstable double bonds in its main chain. It gets deteriorated easily due to ultra violet radiation. Its weather resistance is thus low. For removing this defect, the method of using saturated rubber with almost no double bonds in the main chain is proposed. Acrylic rubber is a representative of this.

[0003] This saturated rubber is stable in ultra violet rays and has excellent weather resistance. However, since it has almost no reactive points, it is not suitable for building graft structure. This causes deformation during molding and so-called weld-dichroism is likely to occur on the surface. Further, diffused reflection is likely to occur at the surface and the luster reduces. Thus the external appearance of molded products is inferior to those of ABS resin.

[0004] For overcoming this difficulty, copolymerization is carried out by selecting a bridging agent or by using peroxide bridging. In such methods, it is possible to increase the bridge density of the acrylic rubber and the external appearance of the product is improved, but as the bridge density increases, the glass transition temperature of the acrylic resin also increases and the impact strength reduces.

[0005] For getting both better impact strength of butadiene rubber and better weather resistance from acrylic rubber, a 2-layered graft polymer rubber obtained by emulsion-grafting of acrylic acid ester and multifunctional group monomer (as bridging agent) on butadiene polymer rubber latex as the core, has been proposed. In this, selection of multifunctional group monomer and method of copolymerization with acrylate ester are important technical factors.

[0006] For example, Patent JP 58-187411 has proposed a method not allowing the polymerization to complete, by stopping the polymerization in the middle. In Patent JP61-155416, aromatic monomer is polymerized in presence of a graft polymer obtained by grafting acrylate ester on butadiene polymer rubber is proposed and in this, polyallyl monomer is used as the multifunctional monomer. Method proposed in Patent JP62-181312 consists of using two different types of multifunctional group monomers as graft crossing and bridging agent during polymerization of acrylate ester. In these methods improvement in impact strength and weather resistance is seen but the defects of acrylic polymer (namely weld-lines in the molded product and low luster) cannot be removed.

[0007] Including ABS resin, most of the impact resistant styrene resins are almost non-transparent. This is because the refractive index of polymer rubber containing butadiene

rubber or acrylate ester rubber as the rubber-component, is very low as compared to that of matrix resin like styrene-acrylonitrile copolymer. This greatly reduces the transparency to visible light. Such non-transparency makes it inferior to transparent resin in brightness and color development, while coloring the resin.

[0008] For removing this defect, methods like bringing the refractive indices of the rubber component and matrix resin as close as possible for improving the transparency, are known. For example a component of high refractive index is graft polymerized in presence of butadiene polymer for increasing the refractive index. A monomer with still lower refractive index is copolymerized while synthesizing matrix resin, for reducing the refractive index of matrix resin. When this method is used, transparency of the resin markedly increases but the high refractive index component used in graft polymerization in presence of butadiene rubber has usually a high glass transition temperature and high refractive index. Thus when refractive index has been given importance, glass transition temperature of the rubber component increases and impact strength of the resin obtained from matrix resin reduces. By improving transparency of the resin, transparency for ultra violet rays also increases and weather resistance reduces.

[0009] For improving weather resistance, impact strength, transparency of resin, luster of the molded product and weld-doichroism, a lot of research work has been carried out in cases where acrylic resin is used as matrix resin. In most of the cases, resin-rubber type thermoplastic resin is made multilayered. For example, in Japanese patents JP58-167605, JP 60-63248, JP3-52910 and US patent No. 4473679, 3-layered structure, in patents JP59-202213, JP62-41241, JP 52-30996, 4-layered structure, in JP63-27516, 5-layered structure have been mentioned. Patent JP55-27576 mentioned the method of blending 3-layered and 4-

layered structures. These methods are effective in case of acrylic resins but they are not sufficiently effective in case of aromatic and especially styrene resins.

[0010] As regards multilayered structure effective for styrene resins, patent JP5-331334 has proposed double layered structure for improving impact strength while JP 5-302009 has mentioned 4-layered basic structure for improving weather resistance and reducing temperature dependence of tenacity. These methods are effective for specific properties but they are not satisfactory for all the properties like weather resistance, impact strength, and luster of molded product, weld-line bichroism and transparency of resin.

[0011] **The problems this invention sought to solve**

The present inventors conducted intensive research for solving the above problems and observed that multilayered styrene built up mainly from aromatic vinyl compounds, acrylic acid esters and multifunctional group monomer can improve the properties. This multilayered styrene resin did not show low impact strength at low temperatures especially at –30°C.

[0012] This invention presents a weather resistant, impact resistant, transparent multilayered resin that gives lustrous molded products without any weld-bichroism, having good impact strength especially at low temperatures and, an improved method of production of multilayered styrene resin.

[0013] **Procedure for solving the problems**

This invention has the following [1] ~ [8] essential points.

[1]: It is concerned with the method of production of multilayered styrene copolymer that consists of the following steps (1) ~ (5) (the composition is such that the quantity of vinyl

silane compound is 0.1 weight % or more in steps (1) ~ (5)), and molded product of the copolymer.

(1): Monomer mixture (a) composed of 40 ~ 99.949 weight % of styrene and 0 ~ 35 weight % of at least one selected from (metha) acrylate ester (having 1 ~ 8 carbon atoms) and vinyl cyanide compound, 0.001 ~ 5 weight % of multifunctional group monomer and 0 ~ 20 weight % of a vinyl silane compound (that can copolymerize with these) is compounded in such a way that glass transition temperature of the copolymer (A) thus obtained by emulsion polymerization is more than 0°C.

(2): Monomer mixture (b) composed of 75 ~ 99.949 weight % of (metha) acrylate ester (having 1 ~ 8 carbon atoms) and 0.001 ~ 5 weight % of multifunctional group monomer and 0 ~ 20 weight % of a vinyl silane compound (that can copolymerize with these) is compounded in such a way that the glass transition temperature of the copolymer (B) thus newly obtained in this step (2) by emulsion polymerization in presence of the copolymer (A) (obtained in step (1) above), is less than 0°C.

(3): Monomer mixture (c) composed of styrene, 0 ~ 99.999 weight % of at least one selected from (metha) acrylate ester (having 1 ~ 8 carbon atoms) and vinyl cyanide compound, 0.001 ~ 99.95 weight % of multifunctional group monomer and 0 ~ 20 weight % of a vinyl silane compound (that can copolymerize with these) is compounded in such a way that glass transition temperature of the copolymer (C) thus newly obtained in this step (3) in presence of the copolymer (B) (obtained in step (2) above), is more than 0°C and the refractive index is in the range of 1.45 ~ 1.60.

(4): Monomer mixture (d) composed of 60 ~ 85 weight % of styrene and 15 ~ 40 weight % vinyl cyanide compound, 0 ~ 15 weight % (metha) acrylate ester (having 1 ~ 8 carbon atoms) and, 0.001 ~ 10 weight % of multifunctional group monomer and 0 ~ 20 weight % of a vinyl silane compound (that can copolymerize with these) is compounded and emulsion-polymerized in presence of the copolymer (C) (obtained in step (3) above), to get new copolymer (D).

(5): Monomer mixture (e) composed of 60 ~ 90 weight % of styrene and 10 ~ 35 weight % of vinyl cyanide compound, 0 ~ 30 weight % (metha) acrylate ester (having 1 ~ 8 carbon atoms) and, 0 ~ 20 weight % of a vinyl silane compound (that can copolymerize with these) is compounded and emulsion polymerized in presence of the copolymer (D) (obtained in step (4) above), to get new copolymer (E).

[0014] [2]: Method of production of multilayered styrene copolymer mentioned in [1] above, in which the composition of respective monomer mixtures (a) ~ (e) from steps (1) ~ (5) per total of (a) ~ (e) is as follows. Monomer mixture (a) 5 ~ 55 weight %, monomer mixture (b) 10 ~ 60 weight %, monomer mixture (c) 1 ~ 20 weight %, monomer mixture (d) 5 ~ 35 weight % and monomer mixture (e) 10 ~ 79 weight %.

[0015] [3] Method of production of multilayered styrene copolymer mentioned [1] or [2] above, in which the particle diameter of copolymer (E) at the end of step (5) is 50 ~ 500 nm.

[0016] [4] Method of production of multilayered styrene copolymer mentioned in any of [1] ~ [3] above, in which the vinyl group of vinyl silane compound is methacryl group or acryl group.

[0017] [5] Method of production of multilayered styrene copolymer mentioned in any of [1] ~ [4] above, in which the silane compound is dimethyl siloxane, phenyl siloxane or methyl phenyl siloxane.

[0018] [6] Method of production of multilayered styrene copolymer mentioned in any of [1] ~ [5] above, in which the multifunctional monomer compounded in steps (1) ~ (4) is at least one selected from the following group-Polyethylene glycol, polypropylene glycol, (metha) acrylate ester of alkylene diol and di-vinyl benzene.

[0019] [7] Method of production of multilayered styrene copolymer mentioned in any of [1] ~ [6] above, in which the multifunctional monomer compounded in step (4) is allyl (metha) acrylate.

[0020] [8] Multilayered styrene copolymer obtained by the method of production of multilayered styrene copolymer mentioned in any of [1] ~ [7] above.

[0021][9]

Molded product of multilayered styrene copolymer obtained by using multilayered styrene copolymer mentioned in [8] above.

[0022] **Application of this invention**

Application of this invention is concretely explained below.

I. Method of production of multilayered styrene copolymer

Method of production of multilayered styrene copolymer of this invention consists of the following steps (1) ~ (5). In case of vinyl silane, the composition is such that the quantity of vinyl silane compound is 0.1 weight % or more in steps (1) ~ (5).

1. Step (1)

In step (1), monomer mixture (a) composed of 40 ~ 99.949 weight % of styrene and 0 ~ 35 weight % of at least one selected from (metha) acrylate ester (having 1 ~ 8 carbon atoms) and vinyl cyanide compound, 0.001 ~ 5 weight % of multifunctional group monomer and 0 ~ 20 weight % of a vinyl silane compound is emulsion-polymerized under specific conditions to get copolymer (A).

[0023] Following can be used as styrene in this invention. Styrene, or monomer mixtures with styrene as the main component such as mixtures with styrene derivatives like α-methyl styrene, chlorostyerne, vinyl toluene; acrylate esters like methyl acrylate, ethyl acrylate, butyl acrylate; methacrylic acid esters like methyl (metha) acrylate, ethyl (metha) acrylate, butyl (metha) acrylate.

[0024] In monomer mixture (a), the proportion of styrene is 40 ~99.999 weight % as against total of monomer mixture (a). Desirable proportion is 95 ~ 99.949 weight %. If styrene is too much or too less, the transparency of the molded product of the multilayered styrene resin reduces and its luster and weld bichroism reduces.

[0025] Examples of (metha) acrylate ester having 1~ 8 carbon atoms are as follows. Methyl (metha) acrylate, ethyl (metha) acrylate, propyl (metha) acrylate, n-butyl (metha) acrylate, t-butyl (metha) acrylate, pentyl (metha) acrylate, isopentyl (metha) acrylate, n-hexyl (metha)

acrylate, 2-methylpentyl (metha) acrylate, 3-methyl pentyl (metha) acrylate, 4-methylpentyl (metha) acrylate, cyclohexyl (metha) acrylate, phenyl (metha) acrylate, 2,3-dimethyl butyl (metha) acrylate, 2,2-dimethyl butyl (metha) acrylate, 3,3-dimethyl butyl (metha) acrylate, n-heptyl (metha) acrylate, 2-methyl hexyl (metha) acrylate, 3-methylhexyl (metha) acrylate, 4-methylhexyl (metha) acrylate, 5-methylhexyl (metha) acrylate, 2,2-dimethylpentyl (metha) acrylate, 2,3-dimethyl pentyl (metha) acrylate, 4,4-dimethyl pentyl (metha) acrylate, 3,4-dimethyl pentyl (metha) acrylate, n-octyl (metha) acrylate, 2-methylheptyl (metha) acrylate, 3-methylheptyl (metha) acrylate, 4-methylheptyl (metha) acrylate, 5-methylheptyl (metha) acrylate, 3-ethylhexyl (metha) acrylate, 4-ethylhexyl (metha) acrylate, 5-ethylhexyl (metha) acrylate. Isomers of all these can be used. Out of these, n-butyl (metha) acrylate and 2-ethylhexyl (metha) acrylate are desirable but n-butyl (metha) acrylate is more desirable. These monomers can be used alone or as a mixture of 2 or more of them.

[0026] In monomer mixture (a), the proportion of (metha) acrylate ester having 1 ~ 8 carbon atoms or vinyl cyanide compound is 0 ~ 35 weight % as against the total of monomer mixture (a). Desirable proportion is 0 ~ 15 weight %. If this is too much, impact strength of molded product of the multilayered styrene resin copolymer reduces.

[0027] Acrylonitrile or methacrylonitrile can be used as the vinyl cyanide compounds in this invention, but acrylonitrile is desirable.

[0028] Examples of multifunctional group monomers that can be used in this invention are as follows. Allyl (metha) acrylate, divinyl benzene or water insoluble polyalkylene glycol (metha) acrylates like ethylene glycol di (metha) acrylate, diethylene glycol (metha) acrylate. Further, trimethylol propane tri (metha) acrylate, 1,6-hexane diol di (metha) acrylate, diallyl

phthalate, triallyl isocyanulate and triallyl cynulate. Out of these, water insoluble polyalkylene glycol di acrylate, alkyl diol diacrylate, and divinyl benzene are desirable. Poly alkylene glycol diacrylate, 1,4-butane diol diacrylate or 1,6-hexane diol diacrylate are still desirable. 1,4-butane diol diacrylate and 1,6-hexane diol diacrylate are still more desirable. These multifunctional group monomers can be used alone or as a mixture of 2 or more of them.

[0029] In monomer mixture (a), the proportion of multifunctional group monomer is 0.001 ~ 5 weight % out of the total (a) and desirable value is 0.05 ~ 2 weight %. If the multifunctional group monomer is too less, transparency of the molded product of multilayered styrene copolymer reduces and if it is too much, the impact strength reduces.

[0030] There is no specific restriction on the vinyl cyanide compound used in this invention as long as it can copolymerize with the monomer mentioned above. The vinyl group is methacryl group or acryl group. Dimethyl siloxane or methyl phenyl siloxane are desirable silane compounds but dimethyl siloxane is still desirable. Specific examples of this are (metha) acrylate with both terminal groups modified by dimethyl siloxane, (metha) acrylate with both terminal groups modified by diphenyl siloxane, (metha) acrylate with both terminal groups modified by methylphenyl siloxane or, these siloxanes with their one end group modified. Out of these, (metha) acrylate with both terminal groups modified by dimethyl siloxane is desirable. It is better that functional group equivalent quantity of the vinyl silane compound is 400 ~ 5000 but the range of 400 ~ 2500 is still better.

[0031] In monomer mixture (a) the proportion of vinyl silane compound in total quantity of monomer mixture (a) is 0 ~ 20 weight % and desirable value is 0.1 ~ 15 weight % and still

desirable value is 0.2 ~ 10 weight %. If vinyl silane exceeds 20 weight %, transparency of the molded product reduces.

[0032] In step (1), above monomer compound (a) is compounded in such a way that glass transition temperature of the copolymer produced is more than 0°C, desirably above 25°C and still desirably above 60°C. To be specific, a definite quantity of this monomer is weighed in a glass beaker, stirred till it becomes uniform and supplied for the polymerization reaction. Then the glass transition temperature of copolymer (A) thus obtained is measured by the method described later. If the glass transition temperature is below 0°C, transparency and impact strength of the molded product of the multilayered styrene resin is likely to reduce.

[0033] In step (1), it is better that the degree of polymerization is more than 80 weight %. More desirable value is 90 weight % or more and still desirable value is 95 weight % or more. If the degree of polymerization is less than 80 weight %, molded product of multilayered styrene copolymer thus obtained has a tendency to show low transparency and impact strength.

[0034] **2. Step (2)**

Monomer mixture (b) composed of 75 ~ 99.949 weight % of (metha) acrylate ester (having 1 ~ 8 carbon atoms) and 0.001 ~ 5 weight % of multifunctional group monomer and 0 ~ 20 weight % of a vinyl silane compound (that can copolymerize with these) is subjected to emulsion polymerization in presence of the copolymer (A) obtained in step (1) to get copolymer (B).

[0035] The (metha) acrylate ester (having 1 ~ 8 carbon atoms) that can be used in step (1) can be used in this step (2) also, in the same way. Out of these, n-butyl (metha) acrylate and 2-ethylhexyl (metha) acrylate are desirable. Still desirable are n-butyl acrylate and 2-ethylhexyl acrylate and still desirable is n-butyl acrylate. These can be used alone or as a mixture of two or more of them.

[0036] In monomer mixture (b), the proportion of (metha) acrylate ester (having 1 ~ 8 carbon atoms) is 75 ~99.949 weight % of the total of monomer mixture (b). Desirable value is 90 ~ 99.93 weight %. If the proportion of (metha) acrylate ester (having 1 ~ 8 carbon atoms) is less than 75 weight %, the impact strength reduces. If it exceeds 99.949 weight %, transparency of molded product of the multilayered styrene resin reduces.

[0037] Multifunctional group monomer that can be used in step (1), can also be used in the same way in step (2). Water-insoluble polyalkylene glycol diacrylate, alkyl diol acrylate and divinyl benzene are desirable. Still desirable are polyalkylene glycol diacrylate, 1,4-butane diol diacrylate or 1,6-hexane diol dialkylate. Still desirable are 1,4-butane diol diacrylate and 1,6-hexane diol diacrylate. These multifunctional group monomers can be used individually or as a mixture of two or more of them.

[0038] In monomer mixture (b), the proportion of multifunctional group monomers is 0.001 ~ 5 weight % of the total monomer mixture (b). Desirable value is 0.02 ~ 1.5 weight %. If the proportion of multifunctional group monomers is less than 0.001 weight %, the transparency of molded product of the multilayered styrene resin reduces. If it exceeds 5 weight %, the impact strength reduces.

[0039] Vinyl silane compound used in step (1) can be used in this step (2) in the same way. Desirable compounds include those with methacryl group or acryl group as vinyl group. Desirable silane compounds are dimethyl siloxane, diphenyl siloxane or methylphenyl siloxane. Dimethyl siloxane is still desirable. Functional group equivalent quantity of vinyl silane compound is desirably 400 ~ 5000 but 400 ~ 2500 is still desirable.

[0040] The proportion of vinyl silane compound in 0 ~ 20 weight % of the total monomer mixture (b). Desirable proportion is 0.1 ~ 15 weight % and still desirable value is 0.2 ~ 10 weight %. If vinyl silane compound exceeds 20 weight %, transparency of the molded product reduces.

[0041] In step (2) the monomer mixture (b) is compounded in such a way that glass transition temperature of the copolymer obtained is less than 0°C, desirably less than –20°C and still desirably less than –30°C. To be specific, a definite quantity of this monomer is weighed in a glass beaker, stirred till it becomes uniform, and supplied for the polymerization reaction. If the glass transition temperature exceeds 0°C, transparency and impact strength of the molded product of the multilayered styrene resin reduces.

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[0042] In step (2), it is better that the degree of polymerization is more than 80 weight %. More desirable value is 90 weight % or more, and still desirable value is 95 weight % or more. If the degree of polymerization is less than 80 weight %, molded product of multilayered styrene copolymer thus obtained has low transparency and impact strength. Here, un-reacted monomer at the end of step (1) is also included in the determination of degree of polymerization.

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[0043] **3. Step (3)**

In step (3), monomer mixture (c) composed of styrene, 0 ~ 99.999 weight % of at least one selected from (metha) acrylate ester (having 1 ~ 8 carbon atoms) and vinyl cyanide compound, 0.001 ~ 99.95 weight % of multifunctional group monomer and 0 ~ 20 weight % of a vinyl silane compound (that can copolymerize with these) is emulsion polymerized under specific conditions in presence of the copolymer (B) (obtained in step (2) above) to get copolymer (C).

[0044] Styrene that can be used in step (1), can also be used in this step (3) in the same manner.

[0045] (metha) acrylate ester (having 1 ~ 8 carbon atoms) and vinyl cyanide compound and multifunctional group monomers that can be used in step (1) or step (2), can also be used in this step (3) in the same manner.

[0046] The proportion of at least one or more compounds selected from the group comprising styrene, (metha) acrylate ester (with 1 ~ 8 carbon atoms) and silane compound in the monomer mixture (c) is as follows. Proportion of styrene is 0 ~ 99.899 weight % (desirably 65 ~ 99.949 weight % and still desirably 75 ~98.1weight %), that of multifunctional group monomer is 0.001 ~ 99.9 weight % (desirably 0.001 ~ 35 weight % and still desirably 1.5 ~ 25 weight %). The proportion of vinyl silane compound that can copolymerize with these, is 0 ~ 20 weight %.

[0047] In step (3), if at least one or more compound from the group of styrene, (metha) acrylate ester (with 1 ~ 8 carbon atoms) and vinyl cyanide is too much, the transparency and

impact strength reduces. It is better that styrene is 40 ~ 99.9 weight %, (metha) acryl ester (with 1 ~ 8 carbon atoms) is 0 ~ 27 weight % and vinyl cyanide compound is 0 ~ 15 weight %. It is still better if styrene is 40 ~ 98.5 weight %, (metha) acrylate ester (with 1 ~ 8 carbon atoms) is 0 ~ 20 weight % and vinyl cyanide compound is 0 ~ 5 weight %. If vinyl cyanide compound or (metha) acrylate ester is too much, the impact strength of molded product of multilayered styrene resin composition becomes less and if styrene is too less, the transparency reduces.

[0048] In step (3), the multifunctional group monomers can be used alone or as a mixture of two or more of them.

[0049] The vinyl silane compound that can be used in step (1), can also be used in step (3). The vinyl group is methacryl group or acryl group. Dimethyl siloxane, diphenyl siloxane or methylphenyl siloxane are desirable silane compounds. Functional group equivalent quantity of vinyl silane compound is desirably 400 ~ 5000 and still desirably 400 ~ 2500.

[0050] In monomer mixture (c), the proportion of vinyl silane compound is 0 ~ 20 weight % in total weight of monomer mixture (c). Desirable value is 0.1 ~ 15 weight % and still desirable value is 0.2 ~ 10 weight %. If the vinyl silane compound exceeds 20 weight %, the transparency of the molded product decreases.

[0051] In step (3), amount of each of the above monomers used in the monomer mixture (c) is such that glass transition temperature of the copolymer (C) thus obtained should be more than 0°C and the refractive index is in the range of 1.45 ~ 1.60. Desirable values of glass transition temperature is 40 ~ 100°C and that of refractive index is 1.50 ~ 1.60. Still desirable

values are 60 ~ 100°C and 1.56 ~ 1.60 respectively. If the glass transition temperature is less than 0°C and refractive index is less than 1.45 or more than 1.60, transparency of the molded product of the multilayered styrene resin composition reduces. To be specific, a definite quantity of this monomer is weighed in a glass beaker, stirred till it becomes uniform and supplied for the polymerization reaction.

[0052] In step (3), desirable value of degree of polymerization is 70 weight % or more. Still desirable value is 80 weight % or more and, still desirable value is 90 weight % or more. If the degree of polymerization is less than 80 weight %, the impact strength and transparency of the molded product of the multilayered styrene resin composition reduce. Here, un-reacted monomer at the end of step (2) is also included in the determination of degree of polymerization.

[0053] **4.Step (4)**

In step (4), the monomer mixture (d) composed of 60 ~ 85 weight % styrene, 15 ~ 40 weight % vinyl cyanide compound, 0 ~ 15 weight % (metha) acrylate ester (with 1 ~ 8 carbon atoms), 0.001 ~ 10 weight % multifunctional group monomer and 0 ~ 20 weight % vinyl silane compound (that can copolymerize with these monomers) is subjected to emulsion polymerization in presence of the copolymer (C) obtained in step (3), to get new copolymer (D).

[0054] Styrene, vinyl cyanide compound, (metha) acrylate ester (with 1 ~ 8 carbon atoms) and multifunctional group monomer used in step (3) can also be used in step (4). Out of multifunctional group monomers, water insoluble polyalkylene glycol diacrylate alkylene glycol diacrylate or allyl methacrylate are desirable. Allyl methacrylate, 1,6-hexane diol

diacrylate or 1,4- butane diol diacrylate are still desirable. These multifunctional group monomers can be used alone or as a mixture of two or more of them. Out of (metha) acrylate esters (with 1 ~ 8 carbon atoms), n-butyl methacrylate, 2-ethylhexyl methacrylate, n-butyl acrylate, 2-ethyl hexyl acrylate are desirable. The most desirable is n-butyl acrylate. These monomers can be used alone or as a mixture of two or more of them. Moreover, (metha) acrylate esters (with 1 ~ 8 carbon atoms) can be compounded further.

[0055] In step (4), vinyl silane compound used in step (1) above, can be used in step (4).

[0056] The composition of each monomer in the monomer mixture (d) in the total monomer mixture (d) is as follows. Styrene 60 ~ 85 weight % (desirably 73 ~ 80 weight %), vinyl cyanide compound 15 ~ 40 weight % (desirably 22 ~ 35 weight %), (metha) acrylate ester (with 1 ~ 8 carbon atoms) 0 ~ 15 weight % (desirably 0 ~ 5 weight %) and multifunctional group monomer 0.001 ~ 10 weight % (desirably 0.1 ~ 5 weight %). If styrene is too much, the impact strength and resistance to chemicals of the molded product of multilayered styrene resin composition reduces. If it is too less, the transparency reduces. If vinyl cyanide compound is too much, the transparency reduces and if it is too less, the impact strength reduces and stability of the latex also reduces. If (metha) acrylate ester monomer becomes too much, the resistance to chemicals and impact strength of the molded product of the multilayered styrene resin composition reduces. If multifunctional group monomer is too much, impact strength of the molded product of styrene resin composition reduces and it is too less, the transparency reduces.

[0057] Proportion of vinyl silane in the monomer mixture (d) is 0 ~ 20 weight %, desirably 0.1 ~ 15 weight % and still desirably 0.2 ~ 10 weight %. If the vinyl cyanide compound is

less than 0.1 weight %, the impact strength at low temperature does not improve but when it exceed 20 weight %, the transparency of the molded product reduces.

[0058] In step (4), above monomer mixture (d) is used in such a way that glass transition temperature of the copolymer (D) thus obtained is desirably more than 60°C. More desirable value is 75 °C and still desirable value is 95 °C. If the glass transition temperature is less than 60°C, impact strength of the molded product of multilayered styrene resin composition reduces.

[0059] In step (4) it is better that the degree of polymerization is more than 70 weight %. More than 85 weight % is better and more than 90 weight % is still better. If the degree of polymerization is less than 70 weight %, the impact strength and transparency of the molded product of multilayered styrene resin composition reduces. Here, un-reacted monomer at the end of step (3) is also included in the determination of degree of polymerization.

[0060] **5. Step (5)**

In step (5), the monomer mixture (e) composed of 60 ~ 90 weight % styrene, 10 ~ 35 weight % vinyl cyanide compound, 0 ~ 30 weight % (metha) acrylate ester (with 1 ~ 8 carbon atoms) and 0 ~ 20 weight % vinyl silane compound (that can copolymerize with these monomers) is subjected to emulsion polymerization in presence of copolymer (D) obtained in step (4), to get new copolymer (E).

[0061] Styrene, vinyl cyanide compound, (metha) acrylate ester (with 1 ~ 8 carbon atoms) and multifunctional group monomer used in step (4) can also be used in step (5). n-butyl methacrylate and 2-ethylhexyl methacrylate are desirable (metha) acrylate esters (with 1 ~ 8

carbon atoms). n-butyl acrylate, 2-ethyl hexyl acrylate is more desirable. The most desirable is n-butyl acrylate. These monomers can be used alone or as a mixture of two or more of them.

[0062] The vinyl silane compound used in step (1) above, can be used in step (5).

[0063] The composition of each monomer in the monomer mixture (e) in the total monomer mixture (e) is as follows. Styrene 60 ~ 90 weight % (desirably 65 ~ 80 weight %), vinyl cyanide compound 10 ~ 35 weight % (desirably 20 ~ 30 weight %) and (metha) acrylate ester (with 1 ~ 8 carbon atoms) 0 ~ 30 weight % (desirably 0 ~ 15 weight %). If styrene is too less, the impact strength and resistance to chemicals of the molded product of multilayered styrene resin composition reduces. If it is too less, transparency of the molded product of the multilayered resin composition reduces. If it is too much, the impact strength reduces. If vinyl cyanide compound is too less, the resistance to chemicals reduces and if it is too much, the transparency reduces. If (metha) acrylate ester monomer becomes too much, the resistance to chemicals and impact strength of the molded product of the multilayered styrene resin composition reduces. If multifunctional group monomer is too much, impact strength of the molded product of styrene resin composition reduces.

[0064] Proportion of vinyl silane in the monomer mixture (e) is 0 ~ 20 weight %, desirably 0.1 ~ 15 weight % and still desirably 0.2 ~ 10 weight %. If the vinyl cyanide compound exceeds 20 weight %, the transparency of the molded product reduces.

[0065] In step (5) it is better that the degree of polymerization is more than 85 weight %. More than 90 weight % is better and more than 95 weight % is still better. If the degree of

polymerization is less than 85 weight %, the impact strength and transparency of the molded product of multilayered styrene resin composition reduces. Here, unreacted monomer at the end of step (4) is also included in the determination of degree of polymerization.

[0066] 6. The quantity of monomer mixtures (a) ~ (e) compounded in monomer compounding steps (1) ~ (5) is as follows, compared to total quantities of (a) ~ (e) respectively. Thus the quantity of monomer mixture (a) compounded in step (1) is desirably 5 ~ 55 weight %, still desirably 10 ~ 45 weight % and still desirably 10 ~ 30 weight %. If the monomer mixture (a) is less than 5 weight %, the transparency of molded product of multilayered styrene resin composition reduces. If it is 55 weight % or more, the impact strength of the molded product reduces.

[0067] In step (2), the monomer mixture (b) is desirably 10 ~ 60 weight %, more desirably 15 ~ 50 weight % and still desirably 20 ~ 40 weight %. If the monomer mixture is less than 10 weight %, impact strength of the molded product of multilayered styrene resin composition reduces. If it is more than 60 weight %, transparency of the molded product reduces.

[0068] In step (3), the monomer mixture (c) is desirably 1 ~ 20 weight %, more desirably 2 ~ 15 weight % and still desirably 4 ~ 10 weight %. If the monomer mixture (c) is less than 1 weight %, transparency of the molded product of multilayered styrene resin composition reduces. If it is more than 20 weight %, impact strength and thermal resistance of the molded product reduces.

[0069] In step (4), the monomer mixture (d) is desirably 5 ~ 35 weight %, more desirably 7 ~ 20 weight % and most desirably 10 ~ 15 weight %. If the monomer mixture (d) is less than 5

weight %, impact strength and resistance to chemicals of the molded product of multilayered styrene resin composition reduce. If it is more than 35 weight %, impact strength of the molded product reduces.

[0070] In step (5), the monomer mixture (e) is desirably 10 ~ 79 weight %, more desirably 30 ~ 65 weight % and most desirably 35 ~ 55 weight % .If the monomer mixture (e) is less than 10 weight %, the salting out after polymerization and operations related to drying of the multilayered styrene resin composition become difficult. Transparency, resistance to chemicals and thermal resistance of the molded product reduce. If it is more than 79 weight %, impact strength of the molded product reduces.

[0071] 7. **Polymerization conditions in emulsion polymerization**

(1) Polymerization temperature

Multilayered styrene copolymer of this invention is prepared by emulsion polymerization. Polymerization temperature during various steps is not different but it is in the range of 40 ~ 100°C. Desirable temperature is, however, selected from the range 50 ~ 80°C.

[0072] (2) Seed polymerization

In the method of production of multilayered styrene resin copolymer of this invention, after step (2) the monomer mixtures of the next steps are added one after the other, and polymerized in presence of the copolymer prepared up to the previous step. Thus, in other words, seed polymerization method is adopted after step (2) onwards. While carrying out polymerization after step (2), it is necessary to select conditions so that particles are not newly formed. The quantity of surface active agent used here should be less than the critical micelle concentration.

[0073] (3) Surface active agent

There is no specific restriction on the surface active agent used in the emulsion polymerization and the usual surface active agents can be used. For example, long chain alkyl carboxylate salts, dialkyl sulpho succinate, alkylbenzene sulphonate can be used. The quantity of such surface active agents should be such that the particle diameter at the completion of emulsion polymerization of step (5) is in the range of 50 ~ 500 nm, desirably 50 ~ 350 nm and still desirably 100 ~ 250 nm.

[0074] (4) Polymerization initiator

As for polymerization initiator, there is no specific restriction and usual initiators can be used. For example, lead peroxide, perborate can be used alone or, as redox initiators by combining with sulphite, lead thiosulphate. Or redox initiators like organic peroxide-ferrous sulphate, organic peroxide and sodium formaldehyde sulfoxylate can be used.

[0075] 8. Multilayered styrene copolymer

(1) Particle diameter

In case of multilayered styrene copolymer of this invention, it is better that the particle diameter at the completion of polymerization in the previous step (5) (copolymer (E)) is in the range of 50 ~ 500 nm. If it is less than 50 nm, the impact strength of the molded product reduces. If, however, it exceeds 500 nm, transparency of the molded product reduces. More desirable range is 50 ~ 350 nm and still desirable range for this is 100 ~ 250 nm.

[0076] (2) Structure of the copolymer

Structure of the multilayer styrene copolymer can be studied in detail, by observation under electron microscope.

[0077] (3) Glass transition temperature of the copolymer

Glass transition temperature (Tg) of copolymers obtained in each step (A) ~ (E) can be determined by conducting the following test (1).

[0078] $$Tg = \sum_{i=1}^{k} m_i \times Tg_i$$

[0079] Where, m_i is mole percent of the i th component in the copolymer, Tg_i is glass transition temperature of the component and i represents serial number conveniently given to the monomer forming the copolymer, and this varies from 1 up to maximum k (total number of types of monomers). Glass transition temperature of i th component except multifunctional group monomers represents glass transition temperature of polymer obtained by bulk (block) polymerization of the respective individual components. In such a case, the measurement of glass transition temperature is defined as the temperature when tan δ shows a peak in dynamic visco-elasticity measurement under the conditions of 5 Hz frequency and temperature gradient of $1^{o}C$/ minute. Glass transition temperature of multifunctional group monomer is defined as the temperature at which the linear expansion coefficient of the polymer obtained by bulk (block) polymerization of the respective individual component varies non-continuously under the conditions of temperature gradient of $1^{o}C$/minute during the linear expansion coefficient measurement. In the calculation of glass transition temperature of polymer (B) obtained in step (2), the calculation is done by assuming that copolymer (B) is obtained in step (2) from a combination of unreacted monomer after completion of step (1) and newly introduced monomer (b) in step (2). The calculation of glass

transition temperature from step (3) onwards was also carried out in the same manner. Determination of composition of unreacted monomer in each step can be done by means of gas chromatography and this method was used in application examples described later.

[0080] (4) Determination of refractive index of the copolymer

Refractive index of the copolymers obtained at each step was determined by using the following formula.

[0081] $$n = \sum_{i=1}^{k} m_i \times n_i$$

[0082] Where, m_i is mole percent of the i th component in the copolymer, n_i is refractive index of the i th component monomer and i represents serial number conveniently given to the monomer forming the copolymer. This varies from 1 up to maximum k (total number of types of monomers). Refractive index of the i th component is measured under conditions of $25 \pm 0.05°C$. Calculation of refractive index of copolymer (B) obtained in step (2) is carried out by assuming that copolymer (B) obtained in step (2) is from a combination of unreacted monomer after completion of step (1) and newly introduced monomer (b) in step (2). The calculation of refractive index from step (3) onwards was also carried out in the same manner. Determination of composition of unreacted monomer in each step can be done by means of gas chromatography and this method was used in application examples described later.

[0083] Multilayered styrene copolymer obtained by the method of this invention can be used alone or as a molded product of multilayered structure styrene copolymer, by fusing and

mixing with styrele-acrylonitrile copolymer, styrene-acrylonitrile-methyl methacrylate copolymer, styrene-acrylonitrile-α-methyl styrene copolymer or styrene-acrylonitrile-phenyl maleimide copolymer. In such case, it is better that the proportion of multilayered styrene resin copolymer is more than 15 weight %. If it is less than 15 weight %, impact resistance of the molded product reduces.

[0084] The multilayered styrene copolymer obtained by the method of this invention can be used by adding appropriate additives like coloring agents or stabilizers. If necessary, it can be used by fusing with other copolymers. It can be used in the production of styrene-acrylonitrile--α-methyl styrene copolymer, styrene-acrylonitrile-phenyl maleimide copolymer without any specific restriction, by using block polymerization, suspension polymerization solution polymerization or emulsion polymerization.

[0085] **Application examples**

This invention is explained below by giving application examples.

[0086] Following appliances or methods were used in the measurements made in application examples and comparison examples.

1. Degree of polymerization: Sampled polymerization reaction mixture was dried under infrared moisture system and the weight of un-evaporated portion was measured. The calculation was made from this value and proportion at the time of preparation by using formula (3).

[0087] Weight % of n layer = $((\alpha \times \beta \div \gamma - \delta) / \varepsilon) \times 100\ \%$ ..... (3)

[0088] Meaning of symbols in formula (3) is as follows.

n: Integer between 1 ~ 5

α: Total amount of reaction mixture existing in the polymerization system at the time of completion of polymerization of step (n)

β: Weight of un-evaporated portion existing in reaction mixture taken at the time of completion of polymerization of step (n)

γ: Weight of reaction mixture taken at the time of completion of polymerization of step (n)

δ: Total weight of un-evaporated portion existing in polymer system at the time of completion of polymerization of step (n-1)

ε: Total weight of the monomer added newly in step (n) and multifunctional group monomer, and un-reacted monomer existing in the polymer system at the time of completion of polymerization of step (n-1)

Further, the value of δ is 0 when (n-1) is 0 and ε is the compounded quantity of monomer mixture (A) added in step (1).

[0089] 2. Particle diameter: Particle diameter of the multilayered latex was measured by using particle size LASER scattering method. For this, Model BI-90 manufactured by BIC Co. was used.

[0090] Izod impact strength: Conducted according to ASTM-D256. Thickness of test piece with notch was 1/8 inch. Measuring temperature was 23± 2°C. The Izod impact strength meter used was manufactured by Toyo Seiki Co.

[0091] 4. Dineshutat impact strength: Conducted according to DIN-53453. Thickness of the test piece with notch was 1/8 inch. Measuring temperature was 23± 2°C. The Izod impact strength meter used was manufactured by Toyo Seiki Co.

[0092] 5. Weather resistance

Measured according to JIS A1415 by using Sunshine weather meter (Model WEL-SUN-HCH, Manufactured by Suga Testing Equipment Co.). The change in hue after exposure of 1000 hours was measured. Change in hue was determined by measuring ΔE, by optical color difference meter (Manufactured by Machbeth Co.).

[0093] 6. Visible optical transparency

Transparency in the wavelength region 400 ~ 800 nm was studied. The value obtained by dividing the area enclosed between transparency curve of the test piece and baseline by that measured in the same way for a matrix resin (that does not contain multilayered structure at all) is considered as the transparency of the test piece. Thickness of the test piece was 2 mm and the measurement was made by using Optical intensity meter (Model 228A, Manufactured by Hitachi Manufacturing Co.), at 23± 2°C.

[0094] 7. Thermal deformation temperature

Measured according to ASTM D-648-56. A test piece of ½ inch was taken and the measurement was made with a load of 18.4 kgf, temperature-increase rate of 2.0± 2°C. The temperature at which the deformation reached 0.26 mm was taken as thermal deformation temperature.

[0095] 8. Tensile strength

Measured according to JIS K6319, by using Tensile test meter (Model UTM-III-500, Manufactured by Orienteck Co.).

Test conditions: Gap between chucks 112 mm± 0.05 mm

Full scale 200 kg

Chart speed 100 mm/minute

Test speed 19 mm/minute

Measuring temperature 23± 2°C

[0096] 9. Color development

Blackness of the molded product was measured with optical color difference meter (Manufactured by Sakata Inks) and it was considered as a measure of color development.

[0097] 10. Luster

Surface luster at angle of incidence of 60° was measured according to JIS Z 8741. For this, a photometer manufactured by Nippon Denshoku Industries (model VG-IB) was used.

[0098] Abbreviations of the compounds used are as follows.

St: Styrene

BuA: Butyl acrylate

AN: Acrylonitrile

MMA: Methyl methacrylate

HAD: 1,6-hexane diol diacrylate

AMA: Allyl methacrylate

V-Si: Methacryl group modified dimethyl siloxane

TDM: t-dodecyl mercaptan

KPS: Potassium persulphate

ASK: Alkenyl succinate potassium

[0099] **Application example 1**

Step 1

1500 g distilled water and 4.03 g ASK were taken in a 4-liter flask equipped with a cooling condenser. The temperature was raised to 40°C while stirring at a speed of 320 rpm. When the temperature reached 40°C, nitrogen gas was passed through it while maintaining the same temperature for about 1 hour, to replace oxygen dissolved in the water by nitrogen. After this, the temperature was raised to 70°C under a current of nitrogen and 25.3 g of aqueous solution of KPS with 1.19 weight % concentration was added. Then a mixture of 344.80 g St, 0.566 g HDA and 12.49 g V-Si (as vinyl silane, viscosity: 58 mm^2/s) was added at the rate of 9.3 g /min. After the addition was complete, it was held at the same temperature for 2.5 hours. The degree of polymerization at this time was 96.5 %.

[0100] **Step 2**

Then 25.8 g of aqueous KPS with concentration 1.1 weight % and 6.04 g of ASK were added and a mixture of 344.80 g BuA and 0.426 g HDA was added at the rate of 9.3 g/min. After the addition was complete, it was held at the same temperature for 2.5 hours. The degree of polymerization of un-reacted monomer mixture at the time of polymerization of step (2) and that from step (1) was 97.7 %. The degree of polymerization of total monomer mixture used in step (1) and step (2) was 98.2%.

[0101] **Step 3**

Then 25.8 g of aqueous KPS of concentration 2.9 weight % was added and a mixture of 63.8 g St, 12.8 g BuA and 1.613 g HDA was added at the rate of 9.3 g/min. After the addition was complete, it was held at the same temperature for 4 hours. Degree of polymerization of un-reacted monomer mixture at the completion of step (2) and the monomer mixture newly added in step (3) (this is called as "degree of polymerization at step (3)") was 98.2 %. The degree of polymerization of total monomer of steps (1) ~ (3) was 99.0%.

[0102] **Step 4**

Then 25.4 g of aqueous KPS of concentration 1.4 weight % was added and a mixture of 104.1 g St, 32.9 g AN and 4.088 g AMA was added at the rate of 9.3 g/min. After the addition was complete, it was held at the same temperature for 1.5 hours. Degree of polymerization of un-reacted monomer mixture at the completion of step (3) and the monomer mixture newly added in step (4) (this is called as "degree of polymerization at step (4)") was 93.0 %. The degree of polymerization of total monomer of steps (1) ~ (4) was 99.2%.

[0103] **Step 5**

Then 25.3 g of aqueous KPS of concentration 1.3 weight % was added and a mixture of 153.34 g St, 40.46 g MMA and 75.31 g AN was added at the rate of 13 g/min. After the addition was complete, it was held at the same temperature for 2 hours. Degree of polymerization of un-reacted monomer mixture at the completion of step (4) and the monomer mixture newly added in step (5) (this is called as "degree of polymerization at step (5)") was 95.5 %.

[0104] Then the entire latex thus obtained was slowly added to 300 g of 1.3 weight % aqueous aluminium sulphate solution at 80 °C while stirring vigorously in about 30 minutes

time and allowed to deposit. After this, it was dried to remove water, to get the required multilayered styrene polymer powder. 430 g of this multilayer polymer powder and 570 g of separately prepared (by suspension polymerization) styrene-acrylonitrile-methyl methacrylate resin (polymer ratio 57/28/15, Hitachi Kasei Industries, ASM 19) and a specific stabilizer were mixed. This mixture was pelletized by using an extrusion machine and the pellets were injection molded to get test samples for the evaluation of performance of molded product.

[0105] **Application example 2**

The procedure was similar to that of application example 1 except that V-Si was not used as vinyl silane compound in step (1) and 15.56 g of it were used in step (2). Degree of polymerization in various steps was as follows. Step (1) 96.8 %, step (2) 97.9 %, step (3) 98.7%, step (4) 98.0% and step (5) 98.2 %.

[0106] **Application example 3**

The procedure was similar to that of application example 1 except that 3.28 g of V-Si was used as vinyl silane compound only in step (4). Degree of polymerization in various steps was as follows. Step (1) 97.1 %, step (2) 96.9 %, step (3) 98.1%, step (4) 98.3% and step (5) 98.9 %.

[0107] **Application example 4**

The procedure was similar to that of application example 1 except that 5.42 g of V-Si was used as vinyl silane compound only in step (4). Degree of polymerization in various steps was as follows. Step (1) 95.8 %, step (2) 96.9 %, step (3) 97.9%, step (4) 98.9% and step (5) 98.9 %.

[0108] **Application example 5**

The procedure was similar to that of application example 1 except that 9.10 g of V-Si was used as vinyl silane compound only in step (5). Degree of polymerization in various steps was as follows. Step (1) 95.4 %, step (2) 96.3 %, step (3) 97.1%, step (4) 98.5% and step (5) 98.6 %.

[0109] **Application example 6**

The procedure was similar to that of application example 1 except that 12.49 g of V-Si was used as vinyl silane compound in step (1), 15.56 g of it was used in step (2), 3.28 g of it was used in step (3), 5.42 g of it was used in step (4) and 9.10 g of it was used in step (5). Degree of polymerization in various steps was as follows. Step (1) 96.1 %, step (2) 95.9 %, step (3) 97.2%, step (4) 97.4% and step (5) 97.9 %.

[0110] **Application example 7**

The procedure was similar to that of application example 1 except that 0.54 g of V-Si was used as vinyl silane compound in step (4). Degree of polymerization in various steps was as follows. Step (1) 97.2 %, step (2) 96.8 %, step (3) 96.5%, step (4) 97.2% and step (5) 95.9 %.

[0111] **Comparison example 1**

The procedure was similar to that of application example 1 except that V-Si was not used in all the steps step (1) ~ (5). Degree of polymerization in various steps was as follows. Step (1) 96.8 %, step (2) 96.2 %, step (3) 97.3%, step (4) 99.5% and step (5) 99.2 %.

[0112] **Comparison example 2**

The procedure was similar to that of application example 4 except that the quantity of V-Si was used in step (4) was 33.9 g. Degree of polymerization in various steps was as follows. Step (1) 97.4 %, step (2) 96.8 %, step (3) 98.7%, step (4) 98.9% and step (5) 99.9 %.

[0113] Composition of monomer mixture compounded in steps (1) ~ (5) in Application example 1 ~ 7 and comparison examples 1 and 2, proportion (weight %) of monomer mixture, degree of polymerization in steps (1) ~ (5) and, glass transition temperature and refractive index of the copolymers are shown in Tables 1 ~ 9.

[0114] Table 1: Results of application example 1

Table 1

	Step 1	Step 2	Step 3	Step 4	Step 5
Composition of monomer mixture (weight %)					
St	96.35	0.0	81.57	73.78	56.97
BuA	0.0	99.88	16.36	0.0	0.0
AN	0.0	0.0	0.0	23.32	27.99
MMA	0.0	0.0	0.0	0.0	15.04
HDA	0.16	0.12	2.07	0.0	0.0
AMA	0.0	0.0	0.0	2.90	0.0
V-Si	3.49	0.0	0.0	0.0	0.0
Compounded monomer mixture (weight %)	29.29	29.29	6.63	11.97	22.82
Degree of polymerization of copolymer (wt %)	96.5	97.7	98.2	98.2	97.9
Glass transition temperature of copolymer (^{o}C)	100.1	-53.4	78.5	98.3	99.3
Refractive index of the copolymer	1.590	1.470	1.567	1.562	1.547

[0115] Table 2: Results of application example 2

Table 2

	Step 1	Step 2	Step 3	Step 4	Step 5
Composition of monomer mixture (weight %)					
St	99.84	0.0	81.57	73.78	56.97
BuA	0.0	95.58	16.36	0.0	0.0
AN	0.0	0.0	0.0	23.32	27.99
MMA	0.0	0.0	0.0	0.0	15.04
HDA	0.16	0.11	2.07	0.0	0.0
AMA	0.0	0.0	0.0	2.90	0.0
V-Si	0.0	4.31	0.0	0.0	0.0
Compounded monomer mixture (weight %)	29.29	29.29	6.63	11.97	22.82
Degree of polymerization of copolymer (wt %)	98.1	96.5	97.1	98.0	96.9
Glass transition temperature of copolymer (°C)	102.5	-54.7	78.5	98.3	99.3
Refractive index of the copolymer	1.592	1.465	1.567	1.562	1.547

[0116] Table 3: Results of application example 3

Table 3

	Step 1	Step 2	Step 3	Step 4	Step 5
Composition of monomer mixture (weight %)					
St	99.84	0.0	78.29	73.78	56.97
BuA	0.0	99.88	15.71	0.0	0.0
AN	0.0	0.0	0.0	23.32	27.99
MMA	0.0	0.0	0.0	0.0	15.04

HAD	0.16	0.12	1.98	0.0	0.0
AMA	0.0	0.0	0.0	2.90	0.0
V-Si	0.0	0.0	4.02	0.0	0.0
Compounded monomer mixture (weight %)	29.29	29.29	6.63	11.97	22.82
Degree of polymerization of copolymer (wt %)	98.5	97.9	96.2	97.5	96.9
Glass transition temperature of copolymer (°C)	102.5	-53.4	76.1	98.3	99.3
Refractive index of the copolymer	1.592	1.470	1.557	1.562	1.547

[0117] Table 4: Results of application example 4

Table 4

	Step 1	Step 2	Step 3	Step 4	Step 5
Composition of monomer mixture (weight %)					
St	98.84	0.0	81.57	71.06	56.97
BuA	0.0	99.88	15.36	0.0	0.0
AN	0.0	0.0	0.0	22.46	27.99
MMA	0.0	0.0	0.0	0.0	15.04
HAD	0.16	0.12	2.07	0.0	0.0
AMA	0.0	0.0	0.0	2.79	0.0
V-Si	0.0	0.0	0.0	3.70	0.0
Compounded monomer mixture (weight %)	29.29	29.29	6.63	11.97	22.82
Degree of polymerization of copolymer (wt %)	97.9	97.1	98.6	96.6	98.4
Glass transition temperature of copolymer (°C)	102.5	-53.4	78.5	96.2	99.3
Refractive index of the copolymer	1.592	1.470	1.567	1.554	1.547

[0118] Table 5: Results of application example 5

Table 5

	Step 1	Step 2	Step 3	Step 4	Step 5
Composition of monomer mixture (weight %)					
St	99.84	0.0	81.57	71.05	55.11
BuA	0.0	99.88	16.37	0.0	0.0
AN	0.0	0.0	0.0	22.46	27.07
MMA	0.0	0.0	0.0	0.0	14.55
HAD	0.16	0.12	2.06	0.0	0.0
AMA	0.0	0.0	0.0	2.79	0.0
V-Si	0.0	0.0	0.0	0.0	3.27
Compounded monomer mixture (weight %)	29.29	29.29	6.63	11.97	22.82
Degree of polymerization of copolymer (wt %)	99.0	98.1	97.5	97.9	95.1
Glass transition temperature of copolymer (°C)	102.5	-53.4	78.5	98.3	97.0
Refractive index of the copolymer	1.592	1.470	1.567	1.562	1.533

[0119] Table 6: Results of application example 6

Table 6

	Step 1	Step 2	Step 3	Step 4	Step 5
Composition of monomer mixture (weight %)					
St	96.35	0.0	78.29	71.05	55.11
BuA	0.0	95.58	15.71	0.0	0.0

AN	0.0	0.0	0.0	22.46	27.07
MMA	0.0	0.0	0.0	0.0	14.55
HAD	0.16	0.11	1.98	0.0	0.0
0.0AMA	0.0	0.0	0.0	2.79	0.0
V-Si	3.49	4.31	4.02	3.70	3.27
Compounded monomer mixture (weight %)	29.29	29.29	6.63	11.97	22.82
Degree of polymerization of copolymer (wt %)	96.8	96.9	98.7	98.8	97.1
Glass transition temperature of copolymer (^{o}C)	102.5	-54.7	76.1	96.2	97.0
Refractive index of the copolymer	1.592	1.465	1.557	1.554	1.533

[0120] Table 7: Results of application example 7

Table 7

	Step 1	Step 2	Step 3	Step 4	Step 5
Composition of monomer mixture (weight %)					
St	99.84	0.0	81.57	73.50	56.97
BuA	0.0	99.88	16.36	0.0	0.0
AN	0.0	0.0	0.0	23.23	27.99
MMA	0.0	0.0	0.0	0.0	15.04
HAD	0.16	0.12	2.07	0.0	0.0
AMA	0.0	0.0	0.0	2.89	0.0
V-Si	0.0	0.0	0.0	0.38	0.0
Compounded monomer mixture (weight %)	29.29	29.29	6.63	11.97	22.82
Degree of polymerization of copolymer (wt %)	97.2	98.3	99.0	97.1	97.8
Glass transition temperature of copolymer (^{o}C)	102.5	-53.4	78.5	97.7	99.3
Refractive index of the copolymer	1.592	1.470	1.567	1.559	1.547

[0121] Table 8: Results of Comparison example 1

Table 8

	Step 1	Step 2	Step 3	Step 4	Step 5
Composition of monomer mixture (weight %)					
St	99.84	0.0	81.57	73.78	56.97
BuA	0.0	99.88	16.36	0.0	0.0
AN	0.0	0.0	0.0	23.32	27.99

MMA	0.0	0.0	0.0	0.0	15.04
HAD	0.16	0.12	2.07	0.0	0.0
AMA	0.0	0.0	0.0	2.90	0.0
V-Si	0.0	0.0	0.0	0.0	0.0
Compounded monomer mixture (weight %)	29.29	29.29	6.63	11.97	22.82
Degree of polymerization of copolymer (wt %)	99.0	98.0	97.5	97.7	98.3
Glass transition temperature of copolymer (^{o}C)	102.5	-53.4	78.5	98.3	99.3
Refractive index of the copolymer	1.592	1.470	1.567	1.562	1.547

[0122] Table 9: Results of Comparison example 2

Table 9

	Step 1	Step 2	Step 3	Step 4	Step 5
Composition of monomer mixture (weight %)					
St	99.84	0.0	81.57	57.48	56.97
BuA	0.0	99.88	16.36	0.0	0.0
AN	0.0	0.0	0.0	18.17	27.99
MMA	0.0	0.0	0.0	0.0	15.04
HAD	0.16	0.12	2.07	0.0	0.0
AMA	0.0	0.0	0.0	2.26	0.0
V-Si	0.0	0.0	0.0	22.09	0.0
Compounded monomer mixture (weight %)	29.29	29.29	6.63	11.97	22.82
Degree of polymerization of copolymer (wt %)	98.3	96.9	97.9	95.4	96.8
Glass transition temperature of copolymer (^{o}C)	102.5	-53.4	78.5	76.5	99.3
Refractive index of the copolymer	1.592	1.470	1.567	1.541	1.547

[0123] Results of tests in Application examples 1 ~ 7 and Comparison examples 1 and 2 are shown in Table 10

Table 10 Evaluation results for Application examples 1 ~ 7 and comparison examples 1 and 2

	Izot Impact strength		Visible transparency	Luster	Color development	Thermal resistance	Tensile strength	Weather resistance
	-30°C	23°C						
	(J / m)		(%)	(%)	(-)	(°C)	(Mpa)	(-)
Appl. Ex. 1	48.5	135.8	72.3	97.6	15.2	90.8	4.87	2.9
Appl. Ex. 2	46.2	136.4	71.6	97.1	15.4	91.3	4.78	2.9
Appl. Ex. 3	49.3	137.9	72.5	97.5	15.4	91.5	4.86	2.9
Appl. Ex. 4	49.3	137.7	72.1	98.5	15.3	90.9	4.77	2.9
Appl. Ex. 5	48.4	133.3	72.2	96.6	15.2	90.0	4.61	2.9
Appl. Ex. 6	49.6	135.6	72.5	96.6	15.4	90.4	4.23	2.8
Appl. Ex. 7	48.6	137.4	71.7	97.5	15.3	90.1	4.05	2.8
Comp.Ex.1	21.4	128.2	72.1	96.1	15.3	90.9	4.54	2.9
Comp.Ex 2	22.5	128.9	71.8	97.1	15.3	90.5	4.61	2.8

[0124] **Effect of this invention**

By the method of this invention, it is possible to produce a multilayered styrene copolymer with excellent weather resistance, luster, thermal resistance, mechanical strength, which can give transparent molded products with good color development and impact resistance properties. Thus this invention presents a multilayered styrene copolymer and its molded product.